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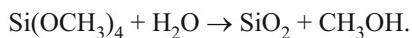
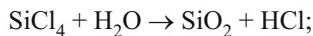
OBTAINING THIN LAYERS OF SILICON DIOXIDE ON QUARTZ

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The possibilities of depositing thin layers of silicon dioxide on the surface quartz are investigated as functions of the chemical composition of the initial reagents and the process conditions. It is shown that silicon chloride and alcoholates can be used for deposition.

Thin nanosize layers of silicon dioxide are deposited on quartz surfaces from the vapor phase in order to be able to bond these surfaces by means of so-called deep optical contacts (DOC) without using additional adhesive reagents.

The main technological operation for obtaining DOC is deposition of a thin coating (silicon dioxide) on a quartz surface in the presence of vapors of silicon-containing compounds (silicon tetrachloride and tetramethoxysilane (TMOS)) and water according to the reactions



The main requirement for the layer deposited is that its surface must be uniform with respect to the presence of heterogeneous impurities — inclusions. Deposition was performed in a volume stainless-steel gas reactor coated on the inside with acid-resistant enamel and fluoroplastic. Quartz plates obtained from blocks grown by the hydrothermal method were used as the substrates for deposition [1].

The surface of the quartz blanks was treated with various alcohols, in order to remove oils and other organic impurities, to prepare it for deposition. Different alcohols — methane, ethanol, and isopropanol purified by rectification in packed columns — as well as reagents produced by domestic and foreign firms were used. The content of metal and organic impurities in the alcohols was $10^{-6} - 10^{-8}\%$ ² and $10^{-2} - 10^{-4}\%$ each. The water content for different samples ranged from 1.00 to 0.05%.

The surfaces were cleaned by washing (in baths) and drying the samples, after which they were rubbed with nonfibrous fabric wetted with alcohol and then subjected to steam-liquid treatment at the boiling point of the alcohols. IR spectroscopy was used to monitor the surface purity. The best results from cleaning the surfaces were obtained by using steam-liquid surface treatment with ethanol and isopropanol with moisture content not exceeding 0.2%.

Samples of silicon tetrachloride from the Aldrich Company (England) which were cleaned by additional rectification and from the “Rea-Éks” firm (Russia) were used for deposition. The content of a number of metal impurities in the silicon tetrachloride sample used for deposition was $10^{-6} - 10^{-8}\%$, and the content of carbon-containing impurities, such as methylchlorosilane, was $10^{-1}\%$ (in the rectification-purified silicon tetrachloride sample from Aldrich) or did not exceed $5 \times 10^{-3}\%$ (in the samples from “Rea-Éks”). Water purified by double distillation in a quartz setup and on ion-exchange resins was used as the source of moisture. Preliminary experiments on additional purification by “sub-boiling” showed no improvement in the quality of the coatings obtained, so that they were not used in subsequent experiments. The content of individual metal impurities in the water likewise was $10^{-6} - 10^{-8}\%$.

TMOS was synthesized by interaction of commercial-grade silicon tetrachloride with methanol in the presence of ammonia and purified by rectification. The content of individual metal impurities in them did not exceed $10^{-6} - 10^{-8}\%$.

The initial water and silicon-containing compounds were evaporated from glass bubblers by feeding nitrogen gas, dried on silica gel and zeolites, into them through rotameters. The growth rate of a layer was monitored continually by the

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² Here and below — content by weight.

optical method using control samples. The required thickness of the layers obtained was 160–250 nm. The optimal growth rate, giving the required quality of the coatings, was 15–20 nm/min.

Using silicon tetrachloride as a source, a quartz coating was deposited on the surface at substrate temperature 20–30°C. It was found using TMOS that deposition on a substrate at an appreciable rate starts at temperature 350–360°C. The optimal deposition temperature was 390–420°C.

The reaction between the silicon-containing components and water occurs mainly in the interior volume of the deposition apparatus, i.e., it is of a homogeneous character. No more than 0.1% of the silicon dioxide formed from the initial silicon-containing reagents is deposited on the surface of an article. The presence of excess components results in undesirable effects, expressed, in particular, as precipitation of amorphous silicon dioxide powder on the surface as a result of the homogeneous reaction in the volume of the apparatus.

To decrease the possibility of this process it was necessary to increase the utilization of the silicon compounds and the maximum deposition of the silicon dioxide on the surface. Experiments on deposition of layers were performed for different values of various process parameters:

- using initial products with different grades of purity;
- thermostating the bubblers at different temperatures;
- changing the feed rate of the carrier gases through the bubblers.

Using silicon-containing samples with different grades of purity revealed that using samples containing higher amounts of metal impurities and carbon-containing substances consistently results in the appearance of a quartz defect on the surface — “dullness,” which can be discerned visually.

The quality of the layers obtained was observed to depend strongly on the ratio of the gases passed through the bubblers with reagents and on the temperature of the bubblers. We attribute this fact to the different degree of saturation of the carrier gas by vapors of the initial components.

Measurements of the rate of outflow of reagents through the bubblers showed that the deposition of the vapor phase of the reagents is a function of the height of the layer of liquid and the sizes of the carrier-gas bubbles. The content of one or another reagent in the carrier gas could vary several-fold. Thus, the level of the liquid in the bubblers and the feed rate of the carrier gas through them must be kept constant in order to obtain reproducible deposition results. Maintaining a constant level of the liquid in the bubblers made it possible to preserve the required stoichiometry of the reagents during the process.

It is evident that the ratio of the partial pressures of water vapor and silicon-containing compounds in the system strongly influences the kinetics of the process. Combined with the change in the degree of saturation of the carrier gas by the initial vapor components, a similar change due to the

TABLE 1.

Sample	Transmission, %, at wavelength, nm			
	200	300	500	900
1	45.5	87.0	96.0	94.0
2	45.1	87.2	96.3	94.2

difference in the character of the saturated vapor pressure dependences of the silicon-containing compounds and water can strongly affect the character of the deposition process. The partial pressures were determined from reference data [2].

The transmission spectra of the quartz samples were studied in the ultraviolet, visible, and infrared ranges. Samples of quartz blanks, used as substrates for depositing thin layers of silicon dioxide from the vapor phase, were investigated in order to determine their suitability for the optimal conditions for obtaining coatings. A M-40 spectrophotometer (Karl Zeiss Company) was used to measure the transmission spectra in the UV and visible regions of the spectrum (200–900 nm).

Since the surface area of samples was smaller than the area of the opening in a standard holder, an unconventional holder was used to measure the spectra.

The transmission of different quartz samples in the range 200–900 nm is virtually identical (Table 1).

The spectra of the samples contain an appreciable absorption band with a maximum at 227 cm⁻¹. A similar band does not occur in the spectrum of a quartz cell from the Karl Zeiss Company. This band is due to an impurity (10^{-3} – 10^{-4} %) which absorbs in the UV range.

A 983 G dual-beam IR spectrophotometer (Perkin Elmer Company) was used to obtain the IR spectra [3]. The differential method was used to record the spectra; the spectrum of the zero line, which was subtracted from the IR spectra of the quartz samples, was stored in memory beforehand.

To determine the range of the measurements, the IR spectra were measured in the range 4000–180 cm⁻¹ for samples with deposited coatings (1–6), obtained using silicon tetrachloride, and for samples (7–13) obtained from TMOS. Total absorption was observed starting at 2300 cm⁻¹ for all samples. In this connection, it was pointless to record the transmission in the range 2300–180 cm⁻¹, and the IR spectra of the samples were obtained in the range 4000–2000 cm⁻¹. The IR spectra of all samples are essentially identical, except in the range 3650–3700 cm⁻¹, and they agree with the published data on the spectra of crystalline silicon dioxide.

The optical properties of quartz articles are presented in Table 2 (4000 cm⁻¹ — start of measurements, 3660 cm⁻¹ — maximum of the absorption band of stretching vibrations of hydroxyl groups, 2650 cm⁻¹ — maximum of the absorption band of overtone vibrations of the silicon–oxygen bond, 2300 cm⁻¹ — start of zero transmission).

TABLE 2.

Sample	Transmission, * %, at wave number, cm^{-1}		
	4000	3664	2650
1	87	0	24
2	88	0	24
3	91	0	25
4	87	0	24
5	88	0	24
6	87	4	24
7	74	7	22
8	89	5	25
9	87	1	22
10	89	3	24
11	92	5	25
12	90	4	26
13	83	2	24

* The transmission of all samples near 2300 cm^{-1} is zero.

Most samples exhibited 87–91% transmission at 4000 cm^{-1} (wavelength 2.5 μm). Sample 7 was an exception; its transmission was 74%. This shows that the samples are highly transparent at 400 cm^{-1} . An intense band with a maximum at 3660 cm^{-1} due to stretching vibrations of the hydroxyl groups OH is characteristic for all samples.

As the data in Table 2 show, zero and low transmission are observed near 3660 cm^{-1} for almost all samples. Low transmission is observed in this region for practically all samples obtained using TMOS. This is probably due to the high content of hydroxyl groups in the experimental samples (possibly $> 0.01\%$). Most samples exhibit 24–25% transmission at 2650 cm^{-1} ; the exceptions are samples 7 and 9 (22%), 3, 8, and 11 (25%), and 12 (26%). That is to say, the transmission at 2650 cm^{-1} differs very little. The presence of weak transmission in this region could be due to the presence of hydrocarbon radicals which were not completely split off on the surface.

For all samples, the region of total absorption in the experimental range of the spectrum starts at 2300 cm^{-1} and continues to 180 cm^{-1} . Compared with the samples of the quartz used in optical cells, absorption bands peaking at 227 nm were recorded in the UV spectra of the samples.

An intense band peaking at 3660 cm^{-1} , due to the stretching vibrations of the hydroxyl groups, was observed in the IR spectra of all samples. Therefore, there is every reason to believe that the quartz used to fabricate the articles contains a large number of hydroxyl groups in the interior volume as well as on the surface of the experimental samples.

The incompleteness of the hydrolysis occurring in the volume of the reactor and on the surface of an article makes it possible for an intermediate layer of silicon oxide with high surface activity to form; this activity is subsequently realized in the creation of DOC with good mechanical properties (rupture strength).

In summary, the quartz used in the technological deposition processes is completely suitable and can give good adhesion of the silicon dioxide layer to the surface of a blank.

This result is very important for obtaining thin layers of silicon dioxide for creating deep optical contacts by this method, since the presence of OH groups on the surface promotes good adhesion on it of the layer of silicon oxide formed during hydrolysis.

In addition, the coatings obtained using silicon tetrachloride and TMOS have essentially the same quality. This makes it possible to choose the initial reagents depending on the structure of the reactor, deposition temperature, and requirements for ecological cleanliness of the process.

REFERENCES

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